Physico-chemical studies on acetaldehyde polymerization at high pressure and low temperature : II. The kinetics of the polymerization of acetaldehyde

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PHYSICO-CHEMICAL STUDIES ON ACETALDEHYDE POLYMERIZATION AT HIGH PRESSURE AND LOW TEMPERATURE

II. The Kinetics of the Polymerization of Acetaldehyde

BY TETUO MIZUKAMI*

It has previously been reported[1] that the high pressure polymerization of acetaldehyde with no catalyst at low temperature took place at the liquid-solid transition of acetaldehyde by pressure. In the present paper, the effects of reaction temperature and pressure on the polymerization rate of acetaldehyde have been studied.

There is the limiting value on the yield of the polymer in the high pressure polymerization of acetaldehyde at each reaction temperature and pressure. The maximum yield is 27.4 weight per cent.

The effect of impurity retarding the polymerization of acetaldehyde is remarkable. For example, when only 0.05 volume per cent of paraldehyde is added to acetaldehyde, the yield of the polymer decreases to only 2.8 per cent of the yield in case of no impurities.

From the initial rate, the values of -6.2, -8.0 and -11.1 ml/mole are obtained as the activation volumes at temperatures -78°C, -70°C and -60°C, respectively. The apparent activation energies are negative values of $-3.17 \sim -4.51$ kcal/mole. Those values increase with pressure. The effect of temperature on the activation volume and the effect of pressure on the activation entropy are satisfied with the equation $(\partial S/\partial P)_T = -(\partial V/\partial T)_P$.

On the other hand, the effect of pressure on the initial rate depends more strongly on the activation entropy than on the activation enthalpy.

The intrinsic viscosity of the polymer is not affected by reaction time and has a constant value at each reaction temperature and pressure. The maximum degree of polymerization of the polymer is about 32,000.

The polymerization of acetaldehyde at high pressure proceeds by the catalytic action of the nucleus of crystal growth of the liquid-solid transition.

Introduction

Letort[2] and Travers[3] reported separately at the same time on the study of the polymerization of acetaldehyde in 1936. Since that time, numerous studies[4] have been carried out on the polymerization of acetaldehyde. This polymerization is roughly divided into three methods.

The first is the freezing polymerization of acetaldehyde which was discovered by Letort and Travers. This method is indispensably necessary to freeze acetaldehyde at -123.5°C of the freezing

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1) T. Mizukami, *This Journal*, **35**, 51 (1965)

2) M. Letort, *Compt. rend.*, **202**, 767 (1936)

3) M. S. Travers, *Tsans. Faraday Soc.*, **32**, 246 (1936)

4) M. Letort et al., *Compt. rend.*, **216**, 58, 608 (1943), **224**, 50 (1947), **231**, 519 (1950), **240**, 86 (1955), **249**, 274 (1954), etc. *J. Chem. Phys.* **48**, 594 (1951), **57**, 752 (1960)

point of acetaldehyde or to condense acetaldehyde vapor on the surface of the vessel being kept below the freezing point. The polymer obtained by this method was presumed as the polyether type polymer by Staudinger[5] and defined by the infrared spectrum by Sutherland[6]. On the other hand, Kargin[7] obtained the same polymer by the radiation induced polymerization of acetaldehyde in solid state.

The second is the catalytic polymerization of acetaldehyde, for example, the alumina catalyst by Furukawa[8], the triethyl aluminum catalyst by Natta[9], the aluminum chloride catalyst by Vogl[10], the aluminum alkoxide catalyst by Furukawa[11], etc. The distinctive characteristic of this polymerization is that the isotactic crystallizable polymer of acetaldehyde, which is not obtained by the freezing polymerization, is obtained.

The third is the high pressure polymerization of acetaldehyde. Novak[12] reported that the polyether type polymer had been obtained by compressing acetaldehyde to the pressure of 9 kb for 24 hours at room temperature, and studied the infrared spectrum of the polymer in detail. On the other hand, Imoto[13] reported that the polyvinylalcohol type polymer was obtained by applying high pressure to acetaldehyde at high temperature in the presence of triethylamine catalyst.

In the previous paper[1], it was reported that the high pressure polymerization of acetaldehyde with no catalyst took place at the liquid-solid transition of acetaldehyde. In this paper, the effects of reaction temperature and pressure on the polymerization rate of acetaldehyde are reported, since the polyether type polymer of acetaldehyde is obtained in a good reproducibility by compressing acetaldehyde to the pressure higher than the limiting pressure at low temperature with no catalyst.

Experimentals

The acetaldehyde used is the same as reported in the previous paper[1], paraldehyde, acetic acid and the other solvents commercially offered as guaranteed reagent are used.

The apparatus used is the same as reported in the previous paper[1], the operations are essentially the same as described in the previous paper[1]. The intrinsic viscosity of the polymer is measured in the solution of methyl ethyl ketone at 27.5°C by using the Ostwald viscometer.

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5) A. Staudinger, *Trans. Faraday Soc.*, **33**, 249 (1936)

6) G. B. B. N. Sutherland, A. R. Philpotts and C. Twiggs, *Nature*, **157**, 267 (1946)

7) V. A. Kargin, V. S. Pshezhetskii and N. A. Bakh, *Visoco*, **3**, 925 (1961)

8) J. Furukawa, T. Saegusa, T. Tsuruta, H. Fujii, A. Kawasaki and T. Tatano, *J. Chem. Soc. Japan, Industrial Chemistry Section*, (*Kogyo Kagaku Zasshi*), **62**, 1926 (1959)

9) G. Natta, *Makromol. Chem.*, **37**, 156 (1960)

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11) J. Furukawa, T. Saegusa and H. Fujii, *J. Chem. Soc. Japan, Industrial Chemistry Section*, (*Kogyo Kagaku Zasshi*), **65**, 695 (1962)

12) A. Novak and E. Whalley, *Can. J. Chem.*, **37**, 1710 (1959)

13) T. Imoto, T. Oota and J. Kamihara, *J. Chem. Soc. Japan, Pure Chemistry Section*, (*Nippon Kagaku Zasshi*), **82**, 492 (1962)

Results

Reproducibility of the experiment

The experiments are repeated four times under the following experimental condition, reaction temperature of $-78°C$, pressure of 5060 kg/cm^2, time of 30 minutes and acetaldehyde of 8 m*l*.

Table 1 Reproducibility of experiment

		Y	$[\eta]$
	1	17.6	5.44
	2	17.6	5.32
	3	18.1	5.44
	4	17.8	5.44
$\bar{x}$	mean value	17.8	5.41
s^2	variance	0.042	0.0027
σ_e^2	unbiased variance	0.056	0.0036
s	standard deviation	0.24	0.052
$s/\bar{x}$	coefficient of variation	0.013	0.0095

Y; the yield of polymer (wt%) $[\eta]$; the intrinsic viscosity (dl/g)

It is said that the polymerization of acetaldehyde is very difficult to perform in a good reproducibility, but the high pressure polymerization of acetaldehyde at low temperature with no catalyst has a good reproducibility as shown in Table 1.

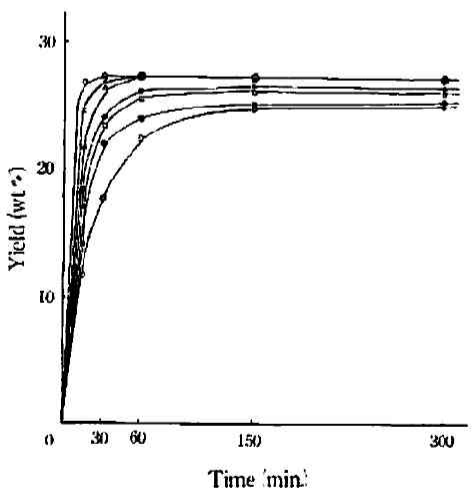

Fig. 1 Yield-time curves at constant temperature ($-78°C$) and various pressures
5060 kg/cm^2 (⊙) 5625 kg/cm^2 (⊗)
6190 kg/cm^2 (□) 6750 kg/cm^2 (●)
7310 kg/cm^2 (△) 7875 kg/cm^2 (×)
8440 kg/cm^2 (○)

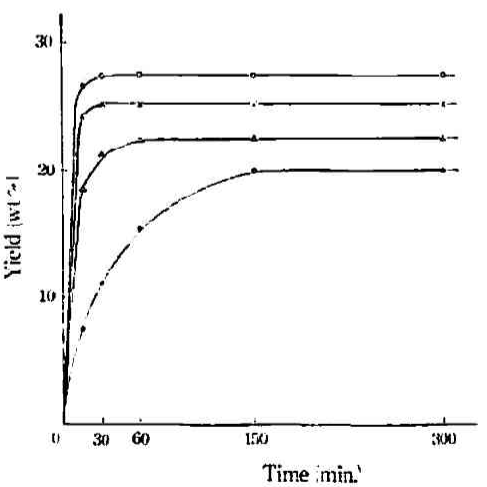

Fig. 2 Yield-time curves at constant pressure (8440 kg/cm^2) and various temperatures
$-50°C$ (●) $-60°C$ (△)
$-70°C$ (×) $-78°C$ (○)

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Effects of pressure and temperature on reaction rate

The experiments are performed at the following conditions:

acetaldehyde	8 m*l* (−78°C)
reaction time	15, 30, 60, 150, 300 minutes
reaction temperature	−50, −60, −70, −78°C
reaction pressure	5060, 5625, 6190, 6750, 7310, 7875, 8440 kg/cm².

Some typical examples of the effects of the reaction temperature and pressure are shown in Figs. 1 and 2. Fig. 1 shows the reaction rate at reaction temperature of −78°C, and at various reaction pressures and Fig. 2 shows the reaction rate at reaction pressure of 8440kg/cm² and at various reaction temperatures. There is the limiting value on the polymer yield as shown in Figs. 1 and 2. The limiting yields of each experiment are shown in Table 2. The intrinsic viscosity of the polymer in methyl ethyl ketone solution is shown in Table 3. This table shows that the intrinsic viscosity is

Table 2 The limiting yield (wt %)

Temperature (°C)	Pressure (kg/cm²)						
	5060	5625	6190	6750	7310	7875	8440
−78	25.2	25.5	26.3	26.5	27.4	27.4	27.4
−70	—	23.9	24.2	24.4	24.3	24.6	25.1
−60	—	—	—	—	21.7	21.9	22.6
−50	—	—	—	—	—	—	20.0

Table 3 The intrinsic viscosity

Temperature (°C)	Pressure (kg/cm²)	Reaction time (min.)				
		15	30	60	150	300
−78	5625	3.72	3.55	3.54	3.62	3.56
	7310	2.98	3.32	3.24	3.24	3.15
	7875	3.04	3.12	2.97	2.97	3.07
	8440	2.85	2.76	2.83	3.05	2.93
−70	5625	4.33	4.55	4.68	4.74	4.35
	7310	3.58	3.78	3.38	3.38	3.65
	7875	3.28	3.12	3.10	3.15	3.41
	8440	3.05	3.11	2.93	2.98	2.95
−60	7310	4.14	3.99	4.08	4.14	3.89
	7870	3.75	3.61	3.65	3.57	3.51
	8440	3.18	3.27	2.99	3.15	3.15
−50	8440	3.56	3.70	3.44	3.44	3.51

independent of the reaction time. That is, the intrinsic viscosity is fixed by reaction temperature and pressure. From the intrinsic viscosity, using Bovey's[14] equation (1), the degree of the

14) F. A. Bovey and R. C. Wands, *J. Polymer Sci.*, **14**, 113 (1954)

$$[\eta]=5.36\times10^{-4}M^{0.65} \quad (1)$$

polymerization is calculated as shown in Table 4.

Table 4 The degree of the polymerization of the polymer

Temperature (°C)	Pressure (kg/cm²)						
	5060	5625	6190	6750	7310	7875	8440
−78	32000	18000	16000	15000	14000	13500	13000
−70	—	25000	21000	20000	17500	15000	13500
−60	—	—	—	—	20500	17500	14500
−50	—	—	—	—	—	—	18000

Effect of solvent

The solution of 4 m*l* acetaldehyde and 4 m*l* solvent is studied on the effect of solvent under the following experimental condition, reaction temperature of −78°C, pressure of 5625 kg/cm², and time of 60 minutes. The solvents studied in this experiment are the following substances, alcohols such as methyl alcohol, ethyl alcohol, etc., ketones such as acetone, methyl ethyl ketone, *etc.*, halogen substituted hydrocarbons such as chloroform, methylene chloride, ethyl chloride, ethyl iodide, etc., aromatics such as benzene, toluene, monochlorobenzene, etc., hydrocarbons such as isopentane, *n*-hexane etc., and triethyl amine, ethyl acetate, ethyl ether, carbon disulfide, carbon tetrachloride, etc. Using solvents of the hydrocarbons the polymerization of acetaldehyde is performed. The polymer is the same as the polymer obtained with no solvents. Table 5 shows the yield and the intrinsic viscosity of the polymer obtained in the presence of solvents.

Table 5 Effect of solvent

Solvent	*Y*	Relative yield	$[\eta]$
non	24.1	100.0	3.54
iso-pentane	20.5	85.1	3.32
n-pentane	21.6	89.6	3.44
n-hexane	21.2	88.0	3.27
cyclohexane	20.3	84.3	3.21
petroleum ether	21.0	87.2	3.35

Effect of impurity

The effects on the polymerization of water, acetic acid and paraldehyde as the impurities in acetaldehyde are studied under the following experimental condition, reaction time of 30 minutes, pressure of 5030 kg/cm² and temperature of −78°C. The results are shown in Table 6. Among those impurities, the retarding effect of paraldehyde on the high pressure polymerization of acetaldehyde is most severe. In the presence of a small amount of paraldehyde, both the yield and the intrinsic

Table 6 Effect of impurity

Impurity	Impurity (vol %)	Y	Relative yield	$[\eta]$
paraldehyde	0.05	0.5	2.8	0.65
	0.1	0.4	2.2	0.45
	0.3	0.3	1.7	0.34
acetic acid	0.05	10.2	56.3	1.00
	0.1	5.7	31.4	0.62
	0.3	3.5	19.6	0.28
water	0.1	15.5	87.0	1.29
	1	15.4	86.5	1.21
	5	14.7	82.5	1.10
	30	13.2	74.1	0.94
	70	4.8	26.9	0.54
non	0	17.8	100	5.44

viscosity are diminished remarkably. It is considered that the difficulty for getting good reproducibility on the yield of linear polymer of acetaldehyde may be owing to this retarding effect of its ring polymers such as paraldehyde and metaldehyde which are easily formed from acetaldehyde. The presence of acetic acid decreases the intrinsic viscosity remarkably. In the presence of water the yield of the polymer is decreased a little but the intrinsic viscosity is diminished remarkably. It is considered that the polymer of low intrinsic viscosity is the polymer of the low molecular weight and of the same structure reported in the previous paper[1].

Considerations

Initial rate

The high pressure polymerization of acetaldehyde has the limiting value on the yield of the polymer as shown in Figs. 1 and 2. The initial rate is determined as shown in Table 7. Using those initial rates, the following discussion is made.

Table 7 The initial rate ($k_i \times 10^4$)

Temperature (°C)	Pressure (kg/cm²)						
	5060	5625	6190	6750	7310	7875	8440
−78	1.68	2.23	2.57	3.17	3.98	4.83	6.47
−70	—	1.33	1.70	2.19	2.88	3.46	4.78
−60	—	—	—	—	1.70	2.36	3.50
−50	—	—	—	—	—	—	2.24

Apparent activation energy

Plotting the logarithm of the initial rate against the reciprocal of the absolute temperature, the linear relation is obtained as shown in Fig. 3. From this slope, the value of the apparent activation energy is obtained as shown in Table 8. The apparent activation energy is negative value and increases with rising reaction pressure.

Table 8 The apparent activation ennergy (kcal/mole)

Pressure (kg/cm²)	5625	6190	6750	7310	7875	8440
E	−4.51	−4.12	−3.78	−3.66	−3.32	−3.17

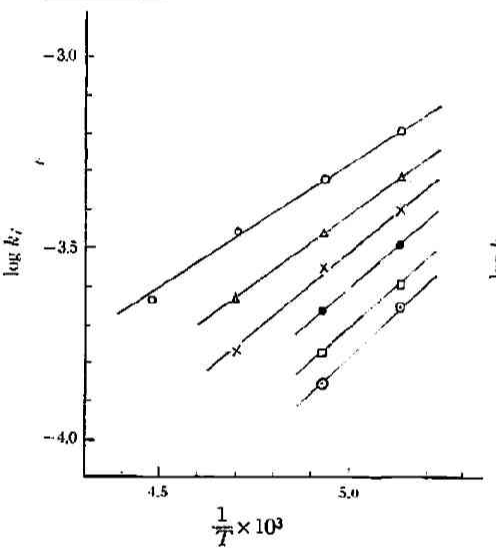


Fig. 3 Effect of temperature on the initial rate at various pressures
5625 kg/cm² (⊙) 6190 kg/cm² (□)
6750 kg/cm² (●) 7310 kg/cm² (×)
7875 kg/cm² (△) 8440 kg/cm² (○)

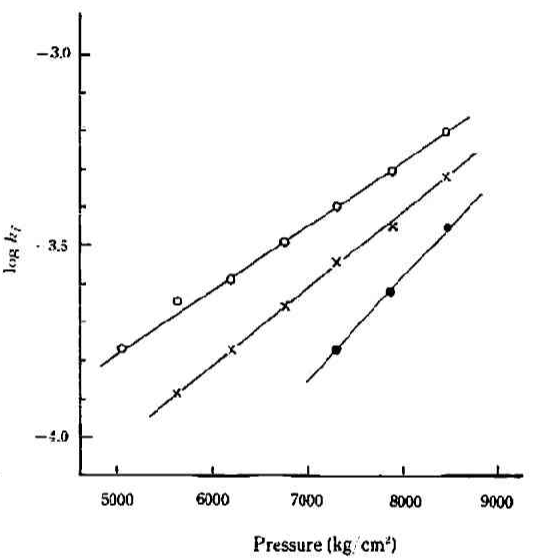


Fig. 4 Effect of presssure on the initial rate at various temperatures
−60°C (●) −70°C (×)
−78°C (○)

Activation entropy

The relation $E \fallingdotseq \Delta H^{\neq}$ being applied the activation entropy at −70°C is calculated from the apparent activation energy and the frequency factor as shown in Table 9. The activation entropy increases with increasing reaction pressure.

Table 9 The activation entropy at −70°C (cal/deg. mole)

Pressure (kg/cm²)	5625	6190	6750	7310	7875	8440
$\Delta S^{\neq}$	−97.2	−95.3	−93.1	−92.1	−90.0	−88.6

The relation of the rate constant, the activation enthalpy and the activation entropy is shown in equation (2), where k is Boltzmann's constant, h is Planck's constant and R is gas constant. It is

$$k=\left(\frac{kT}{h}\right)\exp\left(\frac{-\Delta H^{\neq}}{RT}\right)\exp\left(\frac{\Delta S^{\neq}}{R}\right) \qquad (2)$$

defined that k_1, $\Delta H_1^{\neq}$ and $\Delta S_1^{\neq}$ are corresponding to the pressure P_1 and k_2, $\Delta H_2^{\neq}$ and $\Delta S_2^{\neq}$ to the pressure P_2, the ratio of equation (2) is represented in equation (3). In equation (3), in the case of $P_1 > P_2$ from the experimental results, the first term and the second term are represented as equations (4) and (5).

$$\frac{k_1}{k_2}=\exp\left(\frac{-\Delta H_1^{\neq}+\Delta H_2^{\neq}}{RT}\right)\exp\left(\frac{\Delta S_1^{\neq}-\Delta S_2^{\neq}}{R}\right) \tag{3}$$

$$-\Delta H_1^{\neq}+\Delta H_2^{\neq}<0 \tag{4}$$

$$\Delta S_1^{\neq}-\Delta S_2^{\neq}>0 \tag{5}$$

This indicates that there is the reverse effect between the first term and the second term. On the other hand, the experimental result shows the relation $k_1 > k_2$. In equation (3), k is affected more strongly by the entropy term than by the enthalpy term. This means that the entropy of the system before polymerization is decreased for a large degree with rising reaction pressure and the entropy decrease of the polymerization reaction becomes smaller. Namely, the fact supports that the monomer is aligned by pressure in such a state as the polymerization easily takes place, and the polymerization is accelerated by pressure.

On the other hand, though the entropy decreases of the liquid-solid transition are $-12.3 \sim -9.47$ cal/deg. mole as reported in the previous paper[1] and the activation entropy of ordinary polymerization is some extent of $-20 \sim -40$ cal/deg. mole at most, the activation entropies of this polymerization have large values. This indicates that the polymerization of acetaldehyde takes place at the special field of the liquid-solid interface of acetaldehyde by pressure, and it is necessary for the polymerization that acetaldehyde must have the limiting alignment. From the consideration that the high pressure polymerization is influenced strongly by the presence of the impurities, since those substances disturb the limiting alignment of the acetaldehyde monomer, such explanation as described above seems to be reasonable.

Activation volume

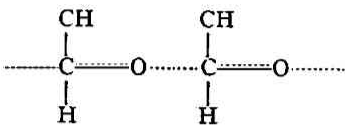
The effect of pressure for the reaction rate is shown in equation (6). Equation (6) becomes equation (7) where k_1 and k_2 are corresponding to P_1 and P_2, respectively.

$$\left(\frac{\partial \ln k}{\partial P}\right)_T=\frac{-\Delta V^{\neq}}{RT} \tag{6}$$

$$\ln\frac{k_1}{k_2}=\frac{-\Delta V^{\neq}(P_1-P_2)}{RT} \tag{7}$$

Plotting the logarithm of the initial rate against reaction pressure, the linear relation is obtained as shown in Fig. 4. From the slope the activation volume is obtained as shown in Table 10. The activation volume decreases with rising reaction temperature. On the other hand, it is considered that those values are reasonable for the activation volume, since the volume decreases of the liquid-solid transition of acetaldehyde are $-4.58 \sim -3.53$ ml/mole and those of the polymerization of acetaldehyde are $-12.1 \sim -13.2$ ml/mole respectively as reported in the previous paper[1].

Assuming that the cross section of CH_3—C—H is not changed in the activated complex, the lengths of C═O····C as shown in (8) are calculated 3.75Å, 3.57Å and 3.27Å at temperatures −78°C, −70°C and −60°C, respectively.



(8)

Those values are rather smaller than the value of 4.36Å which is the sum of the C=O bond length, 1.29Å, and the van der Waals radii of carbon and oxygen atoms, 1.67Å, and 1.4Å, respectively. This means that there must be a definite limiting state for the acetaldehyde monomer for the polymerization. In other words, there must be the limiting alignment of acetaldehyde at the activated state, and then it is considered that the activation entropy has large value.

Table 10 The activation volume (ml/mole)

Temperature (°C)	−78	−70	−60
$\Delta V^{\neq}$	−6.2	−8.0	−11.1

On the other hand, plotting the activation volume against reaction temperature, the linear relation is obtained as shown in Fig. 5, the effect of the temperature on the activation volume is represented as the following relation, $\Delta\Delta V^{\neq}/\Delta T = -0.26$ ml/deg. mole. And Fig. 6 is obtained by plotting the

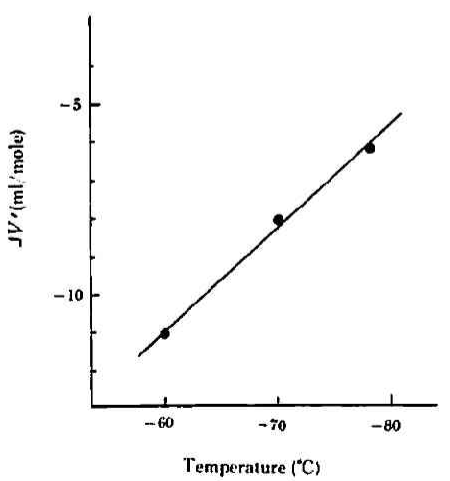


Fig. 5 Effect of temperature on the activation volume

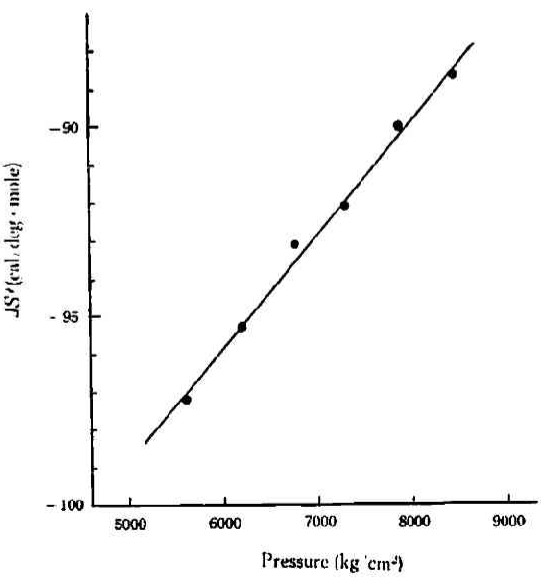


Fig. 6 Effect of pressure on the activation entropy

activation entropy against reaction pressure, the effect of the pressure on the activation entropy is represented as the following relation, $\Delta\Delta S^*/\Delta P=0.20\,ml/\text{deg. mole}$. The relation of equation (9) is satisfied with the values of $\Delta\Delta S^*/\Delta P$ and $\Delta\Delta V^*/\Delta T$, considering the experimental errors. This indicates the appropriateness for the consideration as described above.

$$\left(\frac{\partial S}{\partial P}\right)_T=-\left(\frac{\partial V}{\partial T}\right)_P \qquad (9)$$

Activation free energy

The activation free energy is calculated from the apparent activation energy and the activation entropy and plotted against reaction pressure as shown in Fig. 7. The activation free energy decreases with increasing reaction pressure and this shows that the polymerization easily takes place with increasing pressure.

Effects of reaction temperature and pressure on the intrinsic viscosity of the polymer

The intrinsic viscosity is not changed by reaction time as shown in Table 3. The mean value of the intrinsic viscosity at each reaction temperature and pressure is plotted against reaction pressure and temperature respectively as shown in Figs. 8 and 9. The intrinsic viscosity decreases with in-

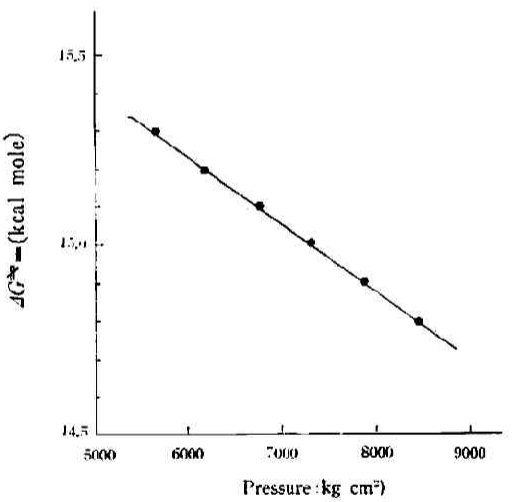


Fig. 7 Effect of pressure on the activation free energy

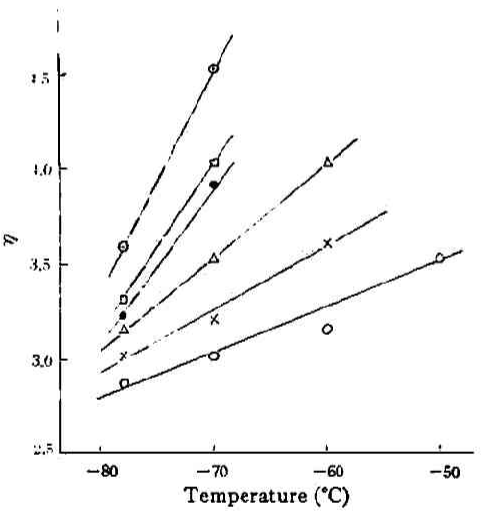


Fig. 8 Effect of temperature on the intrinsic viscosity at various pressures
5625 kg/cm² (⊙) 6190 kg/cm² (□)
6750 kg/cm² (●) 7310 kg/cm² (△)
7875 kg/cm² (×) 8440 kg/cm² (○)

creasing pressure and increases with rising temperature. On the other hand, plotting the logarithm of the initial rate against the logarithm of the intrinsic viscosity, there is a linear relation between the both values as shown in Fig. 10. The relation between the initial rate and the intrinsic viscosity is shown in equation (10). The intrinsic viscosity is proportional to the initial rate to the power of $-1/3$.

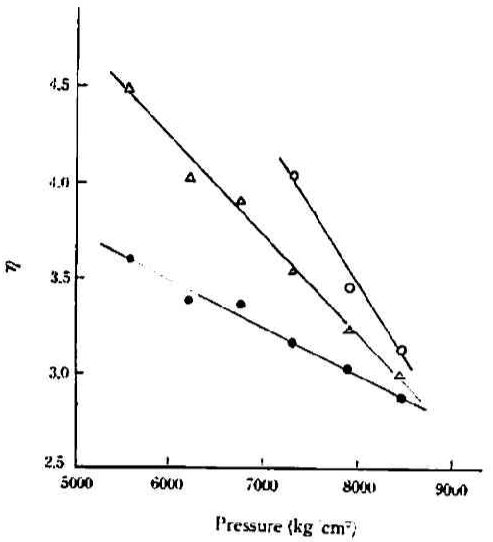


Fig. 9 Effect of pressure on the intrinsic viscosity at various temperatures
−60°C (○) − 70°C(△) −78°C (●)

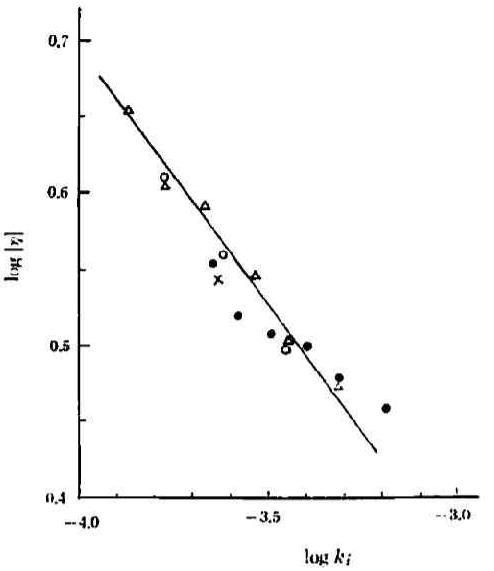


Fig. 10 Relation between the initial rate and the intrinsic viscosity

$$\log[\eta] = -\frac{1}{3}\log k_i - 0.642 \qquad (10)$$

Polymer yield and degree of polymerization

There is a reverse tendency on the relation between the limiting yield of polymer and the degree of the polymerization. Namely, the degree of the polymerization increases with rising reaction temperature and lowering reaction pressure, and the limiting yield of polymer decreases with those factors. However, the degree of the polymerization is affected more strongly by reaction temperature and pressure than the limiting yield is done.

On the other hand, the limiting yield increases with the initial rate, but the increase of the limiting yield is not so large as being considered from the initial rate. At lower temperature and higher pressure, the initial rate of polymerization is accelerated, but the liquid-solid transition which has nothing to do with polymerization is also accelerated. Then, it is considered that the polymerization and the liquid-solid transition of acetaldehyde are affected in the same way by temperature and pressure. For this reason, the degree of the polymerization can not grow to be the large one and the increase of the limiting yield is not so large as being expected from the initial rate.

Effect of solvent

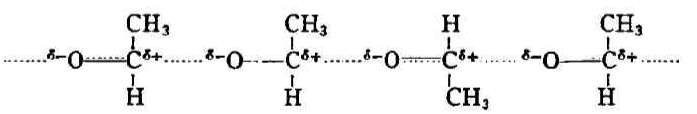
The yield and the intrinsic viscosity in the presence of the solvents of hydrocarbons such as isopentane, *n*-hexane, *etc.*, have a tendency of a little decrease as compared with the case of no solvents as shown in Table 5, but there is little retarding effect on the polymerization with those hydrocarbons solvents. This reason may be that those solvents are mixed homogeneously with acetaldehyde in the volume ratio 1:1 at room temperature, but cyclohexane is separated from acetaldehyde by freezing at −7°C, *n*-hexane and the other three substances are separated from acetaldehyde into two phases

at -13°C and at -25°C, respectively. As the reaction temperature is below -50°C, those substances are separated from acetaldehyde before applying high pressure and a large part of acetaldehyde is compressed in the similar way to the pure state. By this separation, those substances have little retarding effect on the polymerization. As the other solvents can be mixed homogeneously with acetaldehyde under high pressure, they retard the polymerization of acetaldehyde remarkably.

Reaction mechanism

If acetaldehyde is compressed to the pressure higher than the transition pressure, the polymerization and the liquid-solid transition proceed at the same time. It is supposed that the polymerization reaction is initiated with the catalytic action of the nucleus of crystal growth of the liquid-solid transition of acetaldehyde by pressure. The polymerization has the limiting yield of the polymer at each experimental condition as shown in Figs. 1 and 2. This indicates that the polymerization and the liquid-solid transition are proceeding competitively and its ratio is determined by the reaction condition, and after the liquid-solid transition occurs completely, the polymerization does not take place. For example, when acetaldehyde is compressed to a pressure of 5625 kg/cm^2 for 24 hours at -78°C, the yield is 25.3 weight per cent and the intrinsic viscosity is 3.54 dl/g. Those values are essentially the same as those obtained for the reaction time of 150 minutes.

Then, the yield is remarkably enhanced at the initial period of the reaction, and there is the limiting value on the yield as shown in Figs. 1 and 2. The intrinsic viscosity is not affected by the reaction time. The polymerization is affected severely in the presence of the substances mixed homogeneously with acetaldehyde, even if the amount is small. The activation entropies of this polymerization have large values of $-97.2\sim-88.6$ cal/deg. mole, compared with the values of the entropy decreases, $-12.3\sim-9.47$ cal/deg. mole, of the liquid-solid transition of acetaldehyde. In view of the above facts, it is considered that this polymerization takes place only at the limiting alignment of acetaldehyde monomer at the interface of the liquid-solid. Accordingly, any acetaldehyde around the active point of the polymerization is not always capable to polymerize, but the polymerization can occurs only in the presence of the alignment of acetaldehyde monomer with the conjugate form of carbonyl group of acetaldehyde as shown in (11) and as soon as the initiation occurs, the polymeri-



(11)

zation proceeds rapidly.

On the other hand, the liquid-solid transition proceeds at the same time as the polymerization occurs. It is considered that the crystallization occurs at the place where there is not the conjugate alignment of carbonyl group. Therefore the polymerization and the liquid-solid transition of acetaldehyde proceed competitively, and are accelerated by higher pressure and lower temperature in the same way. At higher pressure and lower temperature, the numbers of the nucleus of crystal growth of the liquid-solid transition of acetaldehyde become large. Accordingly, the yield is increased at the initial period of the polymerization, and the intrinsic viscosity decreases with increasing pressure and lowering temperature.

The apparent activation energy of this polymerization is the negative value. This fact is explained from the view that the numbers of nucleus which have the catalytic action for this polymerization increase at lower temperature as described above.

The presence of the substances which disturb the conjugate alignment as shown in (11) retards the polymerization remarkably. The large retarding effect of paraldehyde is explained from the view that the substance disturbs strongly the conjugate alignment of acetaldehyde even if the amount is small. From this consideration, it is assumed that the substances which are mixed homogeneously with acetaldehyde will disturb the conjugate alignment of acetaldehyde necessary for the polymerization. This is comfirmed by the studies of effect of solvents. For example, small amount of acetone and that of methyl alcohol, etc. also have strong retarding effects for the polymerization.

It is considered that the conjugate alignment of acetaldehyde is also disturbed by the presence of acetic acid. The polymer yield is not increased in the presence of acetic acid, though Norrish[15] reported the opposite effect in the freezing polymerization of acetaldehyde.

The presence of water shows the interesting effect. There is an equilibrium between acetaldehyde and water as shown in (12).

$$CH_3CHO + H_2O \rightleftharpoons CH_3CH(OH)_2 \qquad (12)$$

Considering the fact that the substances separated from acetaldehyde before applying high pressure have little retarding effect for the polymerization, it is concluded that diol and free water are separated from acetaldehyde.

The high pressure polymerization of acetaldehyde at low temperature takes place at the interface of the liquid-solid by the catalytic action of the nucleus of crystal growth of the liquid-solid transition by pressure. It seems most reasonable to conclude that this polymerization proceeds according to the ionic conjugate alignment mechanism. It is considered that owing to this mechanism the polymerization is strongly retarded by the presence of the substances which disturb the conjugate alignment of acetaldehyde monomer.

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